AMMONIA-FREE NOx CONTROL SYSTEM

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By

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Abstract

Research is being conducted under United States Department of Energy (DOE) Contract DE-FC26-03NT41865 to develop a new technology to achieve very low levels of NOx emissions from pulverized coal fired boiler systems by employing a novel system level integration between the PC combustion process and the catalytic NOx reduction with CO present in the combustion flue gas. The combustor design and operating conditions will be optimized to achieve atypical flue gas conditions. This approach will not only suppress NOx generation during combustion but also further reduce NOx over a downstream catalytic reactor that does not require addition of an external reductant, such as ammonia.

This report describes the work performed during the October 1 to December 31, 2003 time period.

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1. Executive Summary

Project Overview

State-of-the-art NOx control technology for pulverized coal (PC) steam plants involves a combination of low NOx combustion and selective catalytic reduction (SCR) technologies. Development of these systems has approached a plateau and further improvements will likely be incremental. To advance NOx control technology to the next level, new concepts must be considered.

The objective of this project is to evaluate the viability of a novel integration between the PC combustion process and flue gas NOx reduction. The concept exploits the relationship between CO and NOx both in the combustion and flue gas NOx destruction processes to achieve very low levels of NOx from the boiler system without adding any external reductant, such as ammonia, typically used for SCR processes.

The project starts with a review and evaluation of existing NOx reduction and CO oxidation catalysts, including those catalysts formulations successfully used in the automotive applications, for their use in PC power plants. This knowledge, combined with prior catalyst research for power plant applications conducted at Lehigh University will allow the research team to identify and test catalyst formulations robust enough for power plant flue gas environments and which can achieve competitive NOx reduction performance and economic targets.

A detailed PC combustion study, applying computational fluid dynamics simulation program to performed boiler and burner design modeling, will complement the catalyst study by investigating ways to optimize the combustion process for the lowest NOx formation while generating sufficient levels of CO needed by the downstream catalytic NOx reduction process. Furnace configuration, air staging, and burner design will be optimized in this process.

The study will then focus on the comparative evaluation of a conceptual, 400 MWe, coal-fired PC boiler system, utilizing this novel NOx control concept. For this evaluation, the concept plant will be compared to a traditional PC boiler configured with current commercial low NOx combustion technology and an ammonia-based SCR system. The comparison will involve conceptual level design of the furnace and catalyst reduction system to obtain equipment pricing, operational costs, performance data as well as qualitative reliability information.

Progress During the Quarter

The project work during this quarter is focused on Task 1 – Catalyst Development and Selection. The goal of task 1 is to select candidate catalysts for further experimental characterization. The project team (Foster Wheeler and Lehigh University) held a kick-off meeting on November 5. The work started with a detailed review of existing NOx reduction and CO oxidization catalysts for application in coal fired boilers, based on the following criteria: catalyst activity, deactivation, resistance to inhibitation / poisoning and cost.

During the quarter the work focused on the literature review of catalytic reactions with CO as the reductant. Specifically the work has been concentrated on the automobile industry's experience in NOx reduction and the studies of potentially low cost, base metal catalyst for simultaneous NOx reduction and CO oxidation.

Task 1 - Catalyst Development and Selection will continue in the first quarter of 2004. We also plan to start working on Task 2 – Catalyst testing at Lehigh University.

2. Experimental

The project during this quarter did not involve experimental work.

3. Results and Discussion

Theoretically, there are two ways NOx can be reduced to nitrogen. The first is direct decomposition of NOx to nitrogen and oxygen. Studies of NOx decomposition catalysts have been reported in literature. Catalysts considered include platinum group metals, transition metal exchanged zeolite and base metal oxides. Due to the slow reaction rate and interference with oxygen and moisture in the flue gas, these studies have only limited success and direct decomposition catalysts have not been commercialized.

The second method is NOx reduction by reagent addition. The reagent can be ammonia, such as used in SNCR (high temperature ammonia injection) and SCR (low temperature reduction with catalyst). CO, H_2 and hydrocarbons have also been used as reductants. The catalysts studied for these reduction reactions include precious metals such as platinum, palladium, rhodium and base metal oxides or mix of metal oxides. This method has been successfully used in the automobile industry since the late 1970s. The so-called "Three-way Converter" (TWC) simultaneously reduces NOx, CO and HC emissions. The TWC is used in all passenger cars with conventional gasoline engines sold today in the US [1]. The catalyst is platinum or palladium and rhodium on ceramic or metal substrate. CO functions as the NOx reductant over the rhodium surface according to the following reaction.

$$2NO + 2CO \rightarrow N_2 + 2CO_2 \quad \text{(over metal catalyst)} \qquad (1)$$

The excess CO and the hydrocarbons are oxidized over the platinum/ palladium surfaces. The TWC usually works in the 200 C to 500 C temperature range. High NOx conversion (90-99%) is achievable with this technology. The conventional gasoline engine runs at stoichiometric conditions, controlled by fuel injection. Thus the flue gas will oscillate between slightly oxidizing and slightly reducing conditions at high frequency (usually one cycle in less than a second). To ensure continuous oxygen availability for the CO and HC conversions, cerium oxides, by its REDOX reaction between Ce_2O_3 and CeO_2, have been applied on TWC catalysts to regulate oxygen availability.

The automotive application shows that NOx control with CO as reductant is effective. However, automotive catalysts use mostly precious metals and can be costly for large scale power plant application. Also, these catalysts are inhibited by high oxygen concentrations and poisoned by SO_2, both commonly found in power plant flue gas.

Various mixed oxide catalysts have been considered for the in situ reduction of NO by CO in emission control systems, principally as a replacement for the noble metal based catalysts used in three-ways catalysts. A group of metal oxides of particular interest is the perovskite-type oxide catalysts.

Perovskites are a large family of crystalline ceramics that derive their name from a specific mineral known as perovskite, $CaTiO_3$. Perovskites are among the most abundant minerals on earth. The generic formula for perovskites is ABO_3 or $A_{1-x}C_xBO_3$, where the elements A, B, and C can be a large variety of different elements. Simple perovskites can be easily synthesized, include $SrTiO_3$, $BaTiO_3$, $LaFeO_3$, $BaCeO_3$, and $SrFeO_3$. In these materials with A being a divalent cation, the B element is stabilized in octahedral sites as B4+ between close-packed AO3 layers. This can be visualized as A being on the eight corners of a cube, with B4+ in the center of the cube and the six oxygen atoms being in the middle of the six faces of the cube. These materials can be synthesized by grinding the solid oxides together and calcining at temperatures above 900^{o}C, and thus they are stable in oxygen-containing atmospheres at these high temperatures.

Perovskite materials can be active catalysts, especially if they are synthesized with additional components that enhance the redox properties of the $A_{1-x}C_xBO_3$ materials. Here C is approximately the same size as A or B, partially substituted for either A or B, but has a different valence state than the cation for which it was substituted. This induces a non-stoichiometry in the oxygen content of the material. The activity of the catalysts will then be strongly dependent on the reducing or oxidizing environment of the catalytic reaction of interest. The redox properties of the B cation are important and can determine the lability of the structural oxygen atoms. Since perovskites are relatively low-cost materials and can be both oxidation and reduction catalysts, they were proposed as automotive exhaust treatment catalysts [2]. Most research on the reduction of NO with CO over perovskites has focused on the need to control NO and CO emissions from motor vehicles [3-6]. It has been reported [3,5] that the following sequence of surface reaction steps occurs for the overall reaction to achieve the reaction of NO with CO:

$$NO(g) \rightarrow NO(ads) \quad (2)$$
$$NO(ads) \rightarrow N(ads) + O(ads) \quad (3)$$
$$CO(g) \rightarrow CO(ads) \quad (4)$$
$$CO(ads) + O(ads) \rightarrow CO_2(g) \quad (5)$$
$$N(ads) + NO(ads) \rightarrow N_2O(ads) \quad (6)$$
$$2N(ads) \rightarrow N_2(g) \quad (7)$$
$$N_2O(ads) \rightarrow N_2(g) + O(ads) \quad (8)$$
$$2O(ads) \rightarrow O_2(g). \quad (9)$$

The net desired reaction is complete reaction of the reactants, i.e.

$$2CO + 2NO \rightarrow N2 + 2CO2 \quad (1)$$

A successful catalyst must be designed to inhibit the promotion of N_2O, a greenhouse gas, while having an optimum concentration of adsorbed oxygen on the surface of the catalyst.

In general, the perovskite catalysts studied in the literature provide a wide temperature window for the reduction of NO. Experimental evidence indicates that the catalyst surface is first reduced by CO to create an oxygen vacancy, and then NO adsorption and dissociation occurs.

The latter process takes place at a catalytic site consisting of a redox cation adjacent to the oxygen vacancy. The rate determining step can be the removal of the surface oxygen or the adsorption and dissociation of the NO reactant. Gas-phase components such as O_2, CO_2, and H_2O can inhibit the overall CO + NO reaction by retarding the oxygen removal and by competitive adsorption on the catalyst surface. After dissociation of the NO molecule, rapid mobility and removal of the oxygen is required for high, stable catalytic activity, which again is promoted by cations that readily undergo redox reactions and can function as oxygen transfer/storage components that depends on temperature and gas-phase composition. Examples of the latter active cations in the perovskite structure are Fe and Ce. At low reaction temperatures, N_2O is a dominant product formed from NO, while at high reaction temperature, e.g. >350^{o}C, N_2 is the dominant or only nitrogen-containing product formed. Perovskite catalysts typically are well-defined materials, have high thermal stabilities, and possess low surface areas (5-20 m2/g) that yield low turnover frequencies for the active sites.

4. Conclusion

Task 1 of the project is ongoing. No technical conclusions are currently available.

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